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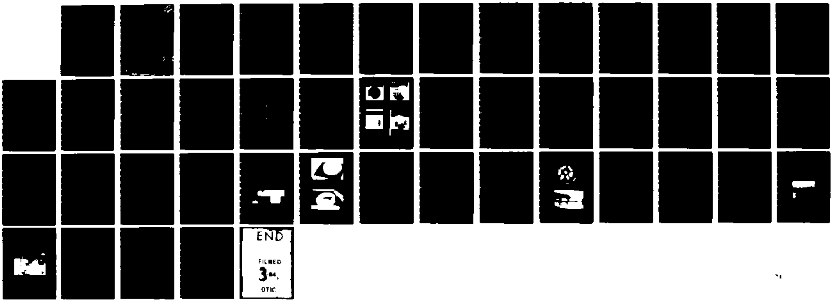

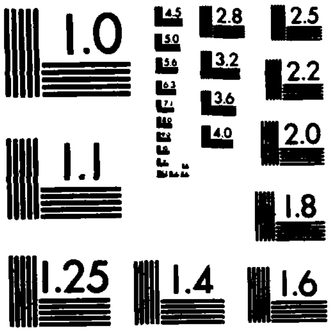

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LARGE PLATE CdTe SYNTHESIS BY SEALED VESSEL TRANSPORT

GEORGE R. CRONIN, PRINCIPAL INVESTIGATOR
(214) 494-5624

QUARTERLY TECHNICAL REPORT NO. 8

REPORT PERIOD: OCTOBER 1 - DECEMBER 31, 1983

SPONSORED BY:

Defense Advanced Research Projects Agency (DOD) ARPA Order No. 4383. Under Contract No. MDA903-82-C-0159 issued by: Department of Army, Defense Supply Service-Washington, Washington, DC 20310

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
AMI-014

2. GOVT ACCESSION NO.
AD-A

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
LARGE PLATE CdTe SYNTHESIS BY
SEALED VESSEL TRANSPORT

5. TYPE OF REPORT & PERIOD COVERED
8th Quarterly Tech.
October 1 - Dec. 31, 1983

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
G. R. Cronin
A. R. Hilton

8. CONTRACT OR GRANT NUMBER(s)
MDA903-82-C-0159

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Amorphous Materials, Inc.
3130 Benton St.
Garland, TX 75042

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Department of Army
Defense Supply Service
Washington, DC 20310

12. REPORT DATE
January 1984

13. NUMBER OF PAGES
37

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Defense Advanced Research Projects Agency
1400 Wilson Blvd.
Arlington, VA 22209

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
APPROVED FOR PUBLIC RELEASE: Distrubution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Cadmium Telluride
Growth of Cadmium Telluride
Large Plates of Cadmium Telluride

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The eighth quarterly technical report for the program to grow large plates of high purity CdTe in a sealed system covers the period Oct. 1-Dec. 31, 1983. A process to grow up to 10 inch diameter plates of high purity CdTe with large grain size has been developed. Evaluation results have confirmed the purity and high resistivity of the resultant materials. During this reporting period plates were grown from near stoichiometric melt compositions up to one inch in thickness. Heat treatment experiments on thick samples under cadmium and tellurium overpressure were carried out. The sawing procedure for cutting oriented substrates was improved

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20. ABSTRACT

by the acquisition of a goniometer for crystal mounting and adapting the orienting laser directly to the wire saw base platform. Also during this reporting period the first experiments in liquid phase epitaxy of HgCdTe were carried out in a modified rotating quartz boat using (111) oriented substrates.

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SUMMARY

The goal of this program is to use vapor transport followed by melt growth to form polycrystalline plates of cadmium telluride (CdTe) 6", 8" and 10" in diameter. The resultant material will be evaluated as substrates for mercury-cadmium-telluride (HgCdTe) growth and as an infrared optical material. Late in the program, mercury vapor will be used in an attempt to grow HgCdTe layers on the large area CdTe plates.

Previous workers have grown large plates of CdTe 6" in diameter transporting the vapor using an inert gas. The starting material was pre-compounded. The initial method used in this program was to compound the material and transport the vapor through a filter into the casting chamber for growth in one operation under vacuum. Solid state recrystallization carried out at high temperatures over a long period of time will produce the desired large grain structure.

Results reported in the first three quarters demonstrated the initial process concept was impractical. Vapor transport of compounded CdTe in a sealed evacuated system was too unpredictable. High temperatures coupled with the presence of cadmium oxide caused a high percentage of quartz failures. Program goals could not be reached with the original process approach. The decision was made to convert to a three chamber quartz system in which the cadmium and tellurium vapors entered the plate chamber from separate tubes.

The new process approach was used repeatedly to produce 6" diameter plates from a stoichiometric melt. Plates weighing almost 2Kgms and possessing the required large grain structure resulted. However, a void region was found to occur between the faces of the plate each time. Growth from solution was used to eliminate this problem. A plate was grown with grains running from the bottom face to the top face from a solution of approximately Cd45 Te55. Total process time was about 72 hours.

The process was applied to the growth of 8" diameter plates successfully. Some changes had to be made particularly with regards to the sequence of reactant distillation. Plates with large grains several inches in area have been grown. Thickness of material is 0.5" or less with the weight of useful material reaching up to 2Kgm. The material has been found to be high purity by emission spectrographic analysis, high resistivity and to exhibit no or little free carrier absorpton in the infrared. Disks may be generated from the plate by cutting out squares followed by edging.

Last quarter marked our first successful attempts at growing 10 inch diameter plates (2) and we also began a series of "seeding" experiments including a return to melts of near stoichiometric composition. A seeded plate, (110), 20cm in diameter and 11mm thick resulted in a 3X improvement in IR transmission at 10 microns. This plate was also grown from a near stoichiometric melt.

A helium-neon laser was obtained for optical orientation purposes and a wire saw was also put into operation for wafering substrates.

During this reporting period one inch thick plates were grown from near stoichiometric melts with no internal voids or vacancies and very little, if any , dendritic growth on the plate surface. This was achieved by closely controlling the freezing direction from bottom to top and from inside to outside simultaneously.

The first heat treating experiments were also carried out this quarter on relatively thick plates and epitaxial layers of HgCdTe were grown on (111) oriented substrates by a liquid phase technique using a rotating boat technique. This report also describes initial attempts of two methods of substrate polishing.

I. INTRODUCTION

A crucial problem in the volume production of U. S. Government FLIR systems is the availability of mercury-cadmium-telluride (HgCdTe) detector arrays. Certainly fabrication of the arrays is difficult but the major problem is the availablity of high quality detector material. The production of bulk HgCdTe alloy is a slow, difficult low yield process. The preferred method to produce detector materials is to grow HgCdTe layers epitaxially on a high quality cadmium telluride (CdTe) substrate. However, the availability of high quality CdTe is also limited. Part of the reason for the shortage is that the conventional method for preparing CdTe crystals is to slowly (0.1"/hour) zone refine small diameter (1") crystals using the Stockbarger technique. The purpose of this program will be to develop an alternative approach.

Large plates of high purity large grain cadmium telluride will be grown in a sealed system. Cadmium telluride will be compounded from the elements, which are sublimed through a filter into a separate growth chamber 6", 8" or 10" in diameter. Grain size will be increased by using a controlled freezing technique. Material thus produced will be evaluated regarding purity, optical homogeneity and suitability as substrates for HgCdTe growth.

II. VAPOR GROWTH OF CADMIUM TELLURIDE

A. General

Cadmium telluride is formed from the group II element cadmium and the group VI element tellurium. All II-VI compounds, as they are called, are difficult to grow because of their high melting points and the fact that both constituent elements are volatile. An appreciable vapor pressure exists for each element at the solid melting point which leads to complications for melt growth. For the same reason, vapor growth of the solid becomes attractive.

Solid CdTe may be grown from the vapor at temperatures considerably below its melting point, 1097° C, according to the following equation:

$$\mathrm{Cd}\ (g) + \tfrac{1}{2}\ \mathrm{Te}_2\ (g) \rightleftharpoons \mathrm{CdTe}\ (s)$$

Where: g signifies gas or vapor
s signifies solid

The reaction as written is reversible which indicates that solid CdTe will sublime or vaporize into its constituent elements. Thus, the source of Cd or Te_2 gas may be either the pure heated elements or a heated source of pre-compounded CdTe solid.

The quality of the CdTe grown from the vapor (or melt) depends upon maintaining the exact ratio of 1:1 between the cadmium and tellurium atoms. The pressure of cadmium vapor (pCd) and the pressure of tellurium vapor (pTe_2) in quilibrium over solid CdTe at the growth temperature is very critical and a function of temperature. Deviations from stoichiometry will occur if the ratios are not closely controlled. Supplying the vapors from pure elemental sources heated separately and mixed together at the reaction site is not too accurate. Even the use of inert carrier gasses does not improve the situation to any great extent. Sublimation of precompounded CdTe followed by removal of the vapor to the reaction site is far more accurate. The compounded material may be weighed to an accuracy of 0.1% or better. The accuracy of the ratios may be maintained through direct sublimation in a closed system or through use of an inert carrier gas in a flowing system.

One quality criteria not mentioned thus far is crystallinity. In melt growth, crystals of one single grain may be grown provided that a seed is used and growth rates are very slow. Such restrictions are also the prime limitation relative to diameter of the crystal. In vapor growth, crystals are grown on other crystal surfaces of the same or similar structure, or they grow on an amorphous substrate with spontaneous nucleation and growth occurring over the entire surface. The first case may produce single crystals provided that growth conditions are carefully controlled. The latter method may produce large grain material provided high growth temperatures are maintained over long periods of time.

B. Previous Work

The first extensive investigation of the preparation of CdTe was carried out by D. de Nobel (1) of Phillips. The physical, optical, electrical and semiconducting properties of the material were characterized. The liquidus -solidus curve and related pressure-temperature studies have served as the basis for melt growth of CdTe over the years. Discussions related to melt growth will not be repeated here only as they are relative to vapor growth.

L. R. Shiozawa and co workers at Gould (now Cleveland Crystal Laboratories) carried out an extensive investigation beginning in the late 1960's concerning the vapor growth of II-VI compounds generally (2) and cadmium telluride (3) specifically. Diagrams from their papers will be used to discuss the problems involved in vapor growth of cadmium telluride.

Figure 1 shows the simple binary phase diagram of the Cd-Te system (2). The diagram indicates a single compound is formed, CdTe, which has a congruent melting point of 1092 °C. The term "congruent melting point" indicates that except at perfect stoichiometry, below the 1092 °C melting point, both Cd rich and Te rich liquids exist in equilibrium with pure CdTe.

The pressure of cadmium at the cadmium rich boundary stability field as a function of temperature (2) is shown in figure 2. The tellurium rich boundary (2) is shown in figure 3. In both diagrams, the data is compared to the pressure for the pure element, P Cd (1) and P Te2 (1). For the low temperature, the measured values are very close to those for the pure liquid or close to those corrected according to RAOULT's Law. RAOULT's law states the vapor pressure of a component is lowered by its atomic fraction in a liqiud mixture:

$$P\,Cd = x\;P\,Cd\,(1)$$

Where P Cd is the pressure of cadmium above the the melt
P Cd (1) is the pressure of pure cadmium at the temperature of measurement
X is the atomic fraction of cadmium in the melt.

A similar statement may be made for the pressure of tellurium. The calculated curves using X are a simple application of RAOULT's law. Those using the Z subscript indicates that association between the atoms in the liquid are taken into account. The curves labeled with the M subscript correspond to the minimum pressure conditions which exist with only pure Cd Te solid present.

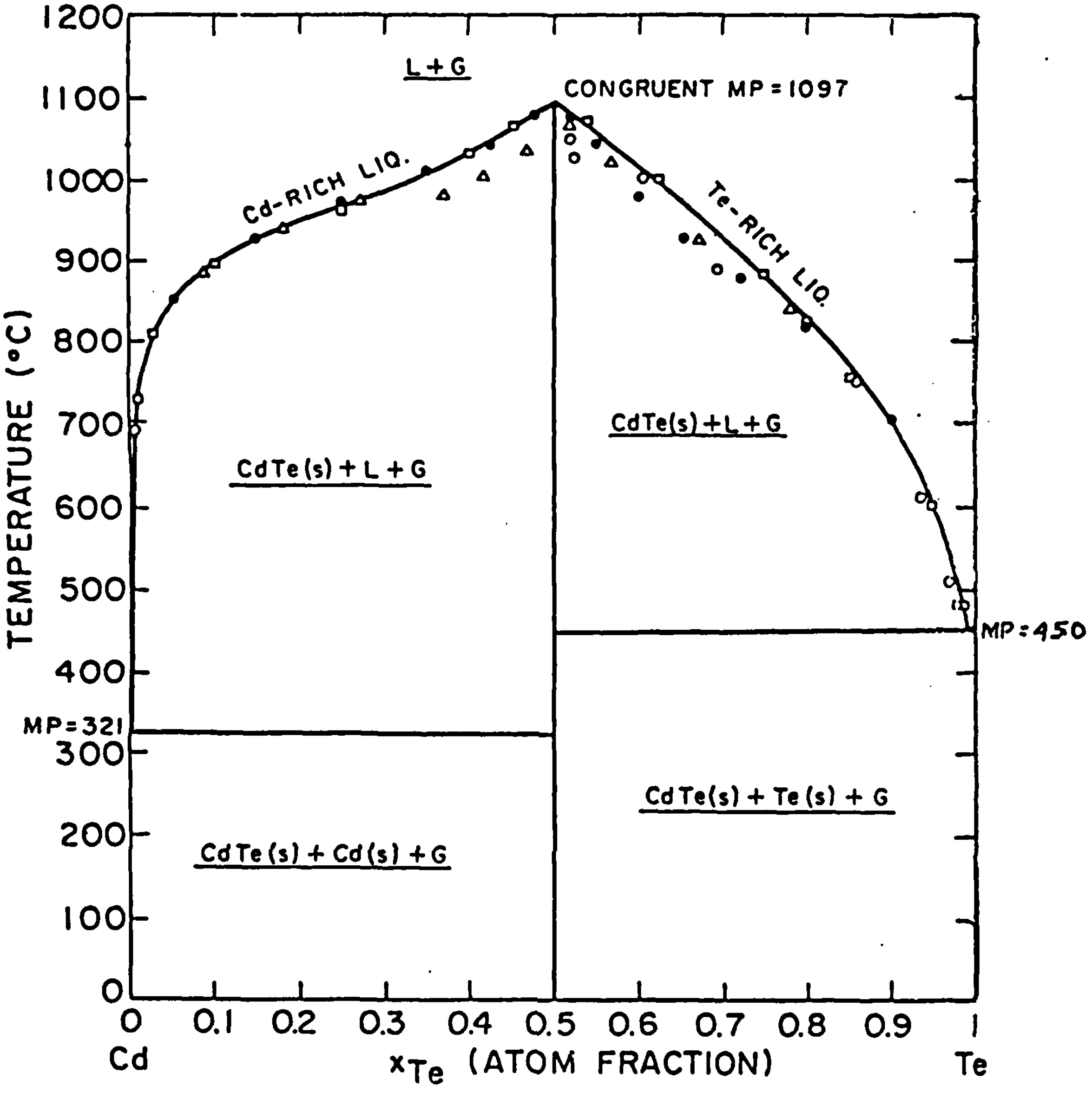


FIG. 1 PHASE DIAGRAM OF THE Cd-Te SYSTEM.

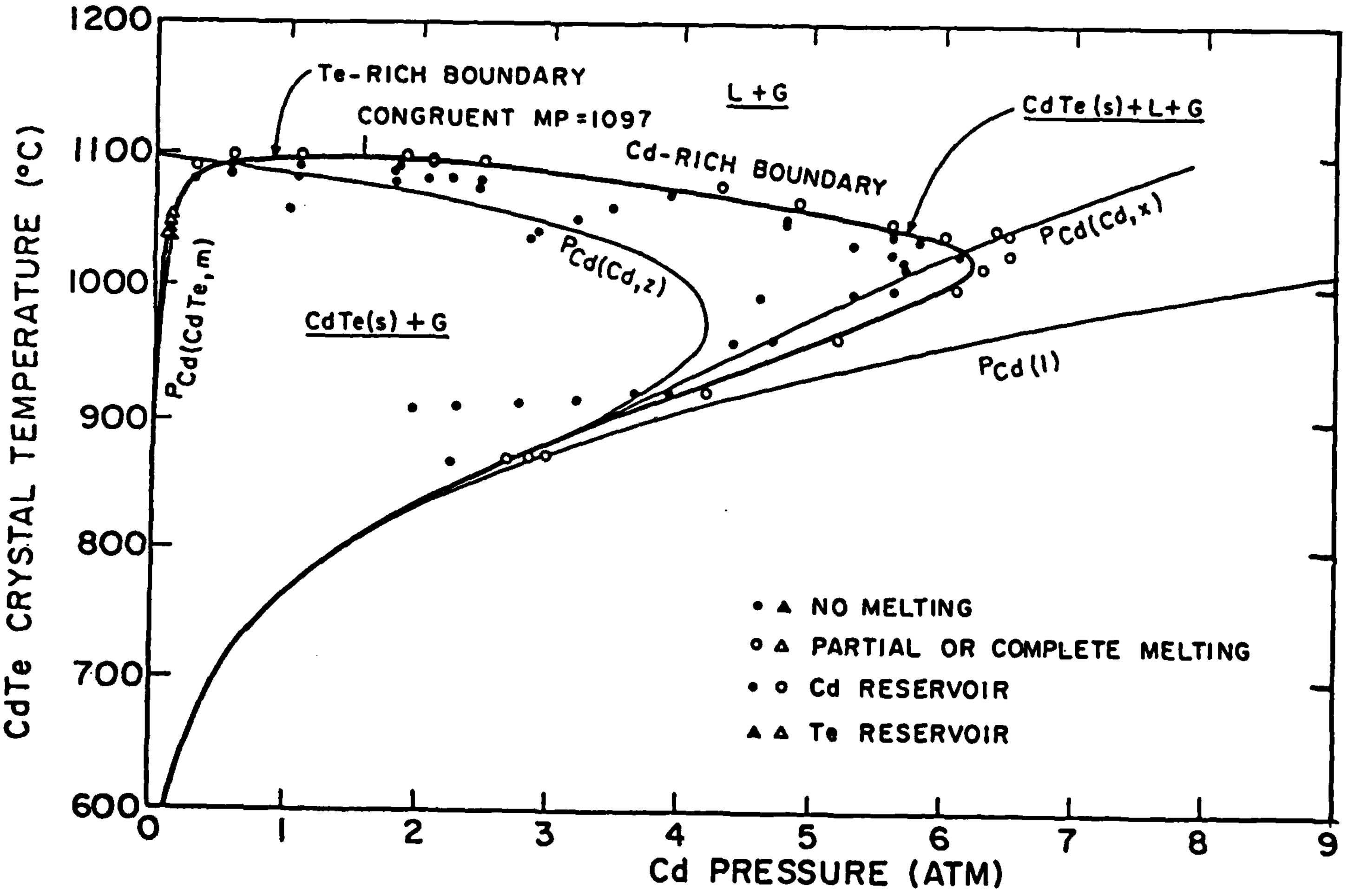


FIG. 2 Cd-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

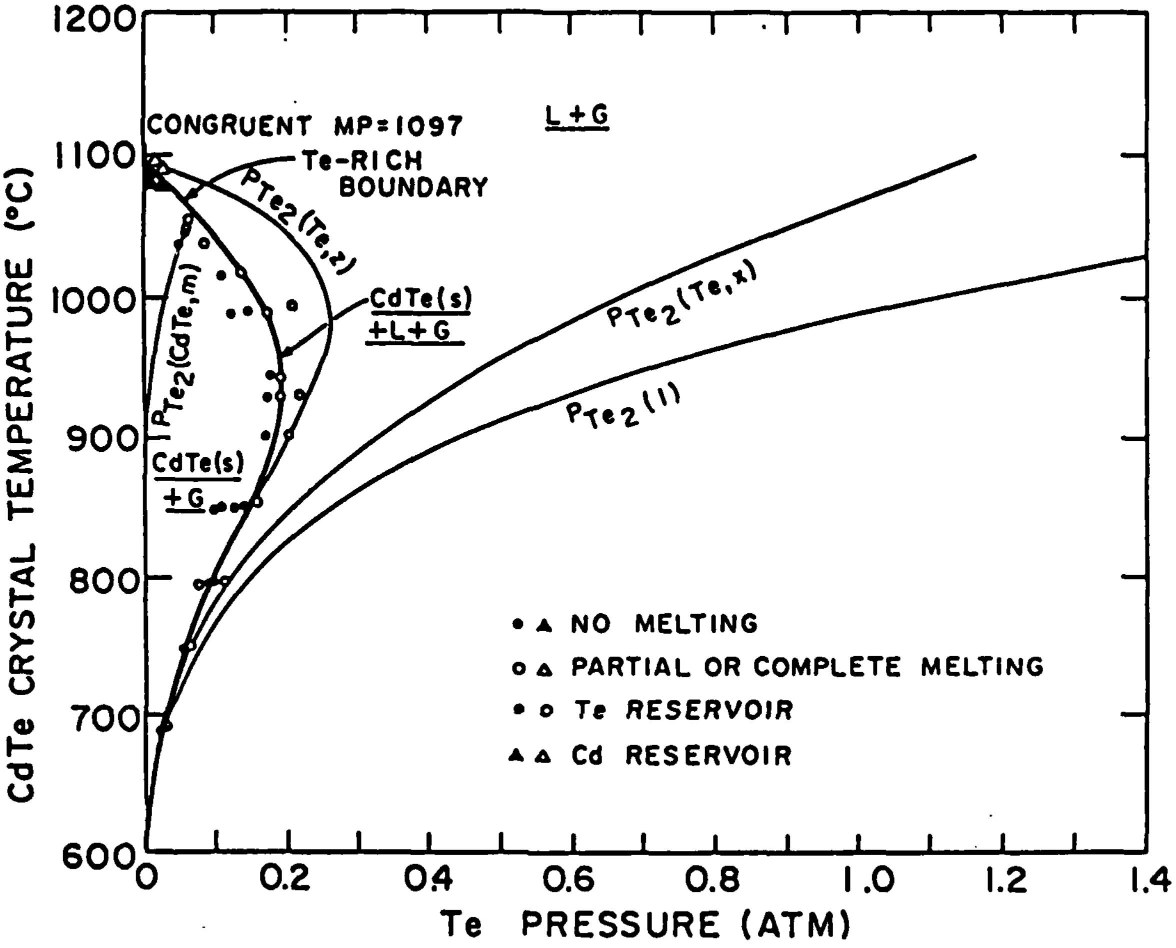


FIG. 3 Te-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

The diagrams indicate that the pressure of cadmium may become very large, 4-6 atmospheres, around 1000 ° C when compounding cadmium telluride. The pressure at the congruent melting point, 1092° C, is about 0.65 atmospheres. The vapor pressure of tellurium is quite low throughout the compounding range. The trick to compounding without an explosion is to stay close to the perfect stoichiometry point and allow time for the liquid phases to become small in quantity. The trick in vapor growth is to be sure that the subliming material is near the stoichiometric ratio so that the resulting vapors are close to the proper ratio. Maintenance of the proper ratio during vapor growth is complicated by the fact that tellurium exists as a diatomic gas, Te_2. The effusion rate for a gas is inversely proportional to the square root of its molecular weight and directly proportional to its pressure. Therefore, for CdTE sublimation, we find the effusion ratios to be (2).

$$R\,Cd/R\,Te_2 = (PCd/PTe_2)\quad(MW\,Te_2/MW\,Cd)^{\frac{1}{2}}$$

Where
R is effusion rate
P is pressure
MW is molecular weight

Even though the vapor starts out at the perfect 2/1 ratio, the cadmium atoms move faster changing the effusing gas mixture ratio. For Cd Te, the ratio becomes 1.33 instead of 2. Build up of the excess component may limit the deposition rate in sealed systems where equilibrium type conditions may be established. The equilibrium constant is given by:

$$K\,Cd\,Te(s) = (PCd)\quad(p\,Te_2)^{\frac{1}{2}}$$

The build up of one component over the other shifts the equilibrium and suppresses further sublimation. Some have used capillary tubes to allow the excess component build up in the vicinity of the source to be pumped away or eliminated. Others have used a carrier gas to carry the subliming vapors, with perfect ratios, to the deposition surface.

C. Vapor Growth of CdTe Plates

Shiozawa (3) and co-workers at Gould used physical vapor deposition (PVD) to grow CdTe plates up to 6" in diameter. Figure 4 illustrates the type of system used. Pre-compounded CdTe was sublimed from the hot zone of a furnace to a slightly cooler zone. Best results were obtained when growth temperatures of 1000-1050° C were used. Recrystallization was allowed to occur over periods up to 400 hours (17 days).

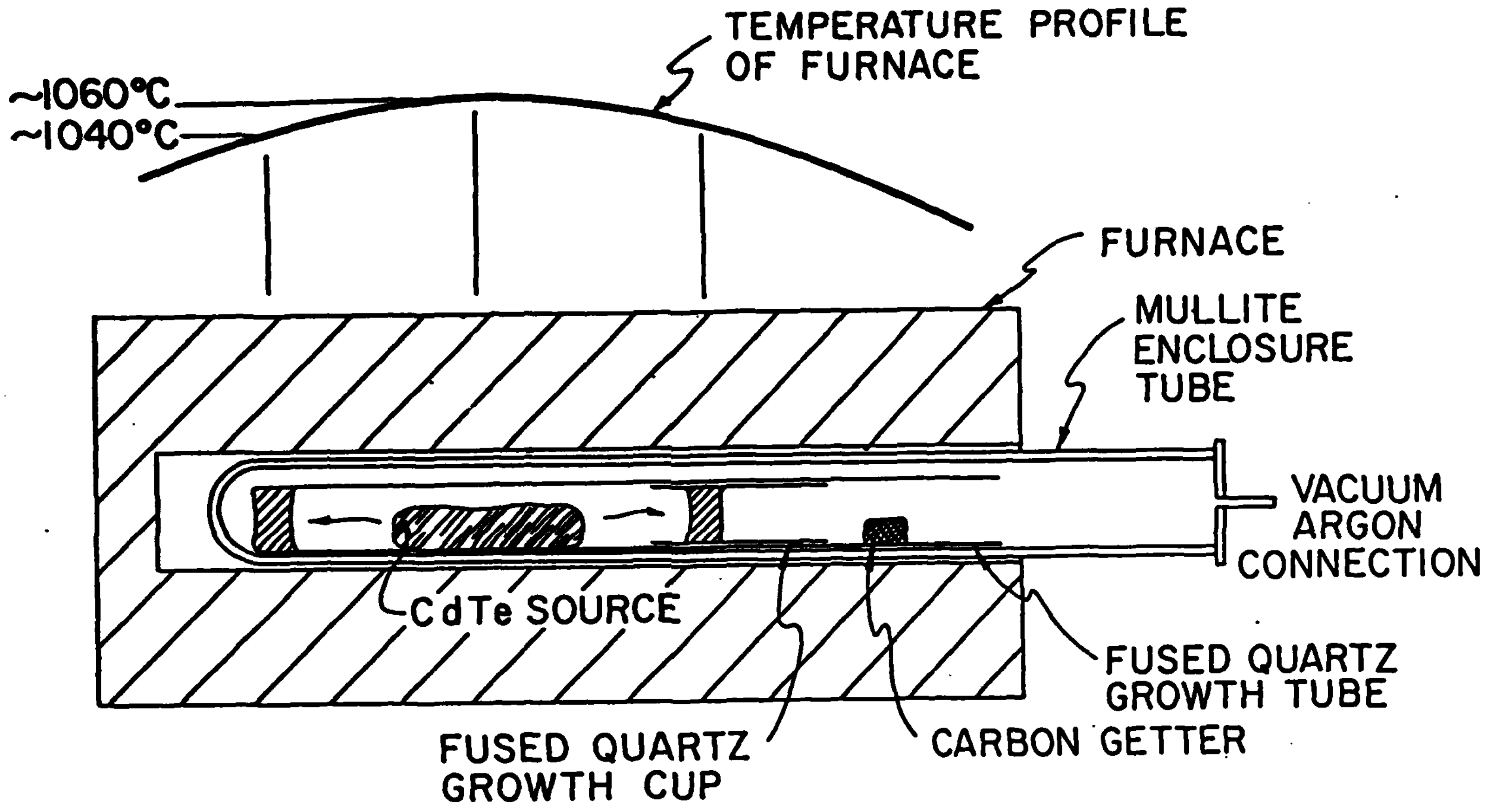


FIG. 4 HORIZONTAL SYSTEM FOR CRYSTAL GROWTH BY GRAIN GROWTH

Figure 5 illustrates the type of grain sizes which were obtained. Growth and recrystallization at 950° C produced small grains. Fast depostion and short growth periods even at the high temperatures produced plates with small grains and voids.

The systems were operated semi-sealed. Argon gas was used as a carrier. Pressures up to 1 atmosphere was used but 180mm, the vapor pressure of stoichiometric CdTe at 1050 °C, was the preferred pressure. Later versions of the system used graphite parts to minimize the effects of air leaks. Also, inert gas was flowed through the furnace to protect the graphite components.

Plates thus produced were heat treated with both Te and Cd vapors at temperatures of 700-800° C. Treatments were alternated and lasted 1-5 days. Measured absorption at 10.6um was 0.001-0.002 cm^{-1}. The effect of heat treating on the infrared transmission of one of their CdTe plates is shown in figure 6. From the transmission for Cd treatment alone, one can see that dual treatment is necessary. After treating with Te_2 vapor, almost theoretical transmission was obtained.

III. APPLICATION OF THE AMTIR METHOD TO THE GROWTH OF CdTe

A. Preparation of AMTIR-I glass

A simplified diagram depicting the glass compounding and casting process developed by Amorphous Materials, Inc. to produce AMTIR-I, is shown in figure 7. A high purity container is placed in a dual zone resistive heated furnace. Zone 1 contains the round empty chamber which will serve later in the process as the casting mold. Zone 2 contains the glass compounding chamber. The process employed at Amorphous Materials combines all three glass processes (element purifications, compounding the glass and casting the plate) into a single continuous process.

In the first step, both chambers are evacuated and heated to remove moisture. A small amount of aluminum wire is added to the elements to act as a getter of oxides in the molten glass. After several hours, the chamber is sealed off while still under vacuum by heating and collapsing the pumping tube. The furnace is closed and need not be opened again until the glass is quenched.

The temperature is raised in both chambers while rocking the furnace. The casting chamber is heated to prevent premature transfer of the elements from the compounding chamber. The furnace is rocked for several hours to insure that all the elements have reacted properly and are uniformly mixed.

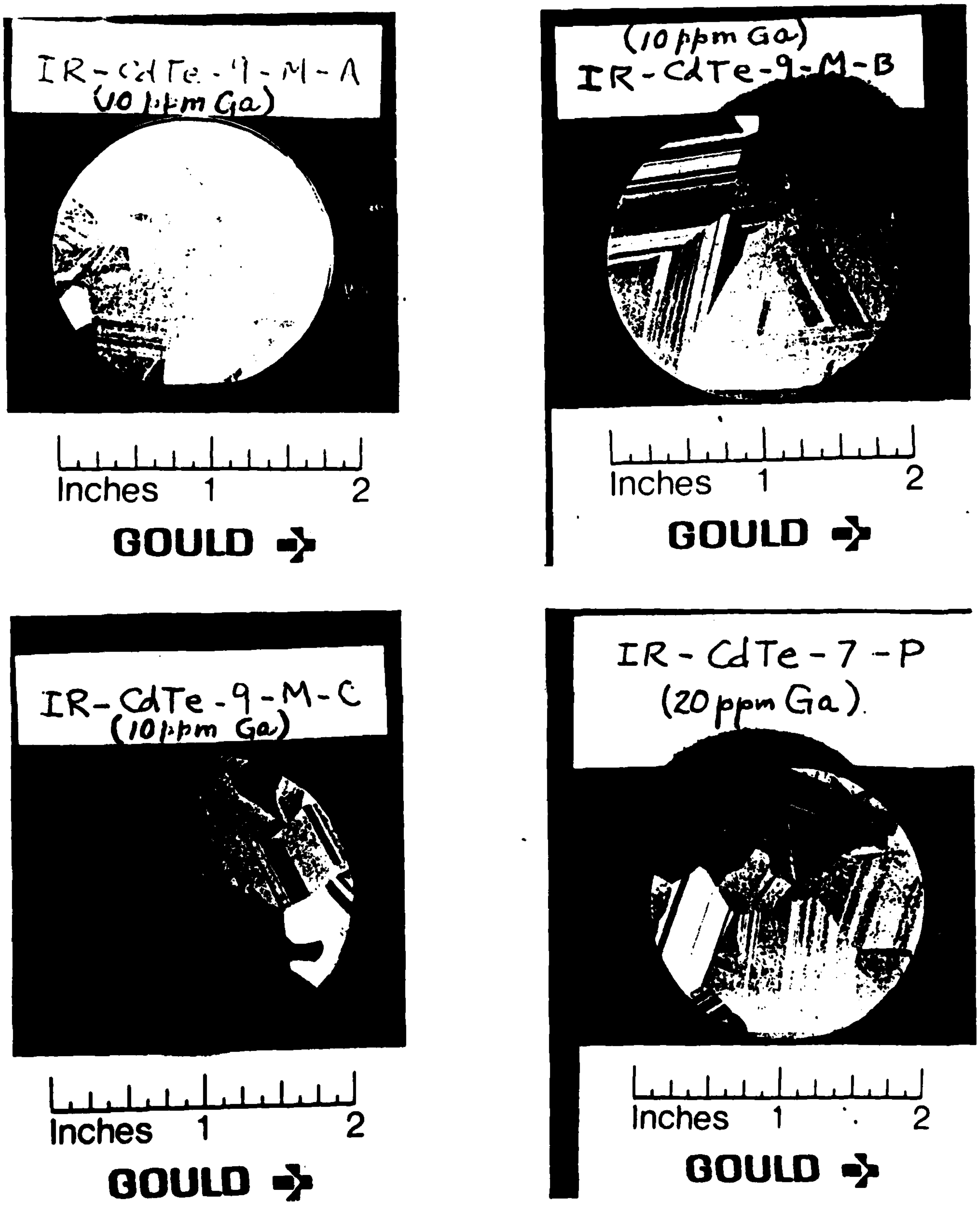


FIG. 5 Lapped Surfaces of CdTe Window Blanks Highlighting Grain and Twin Patterns.

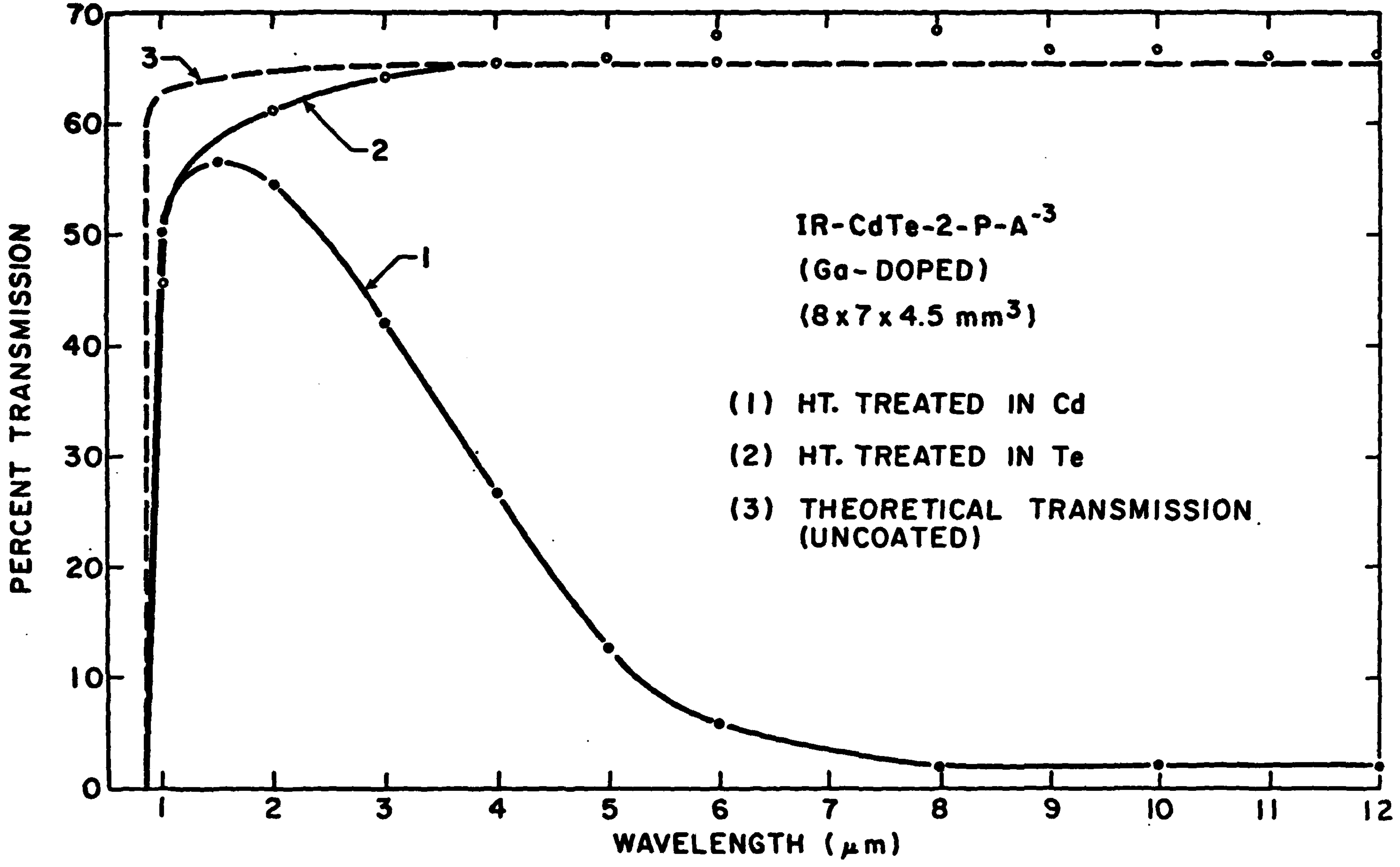
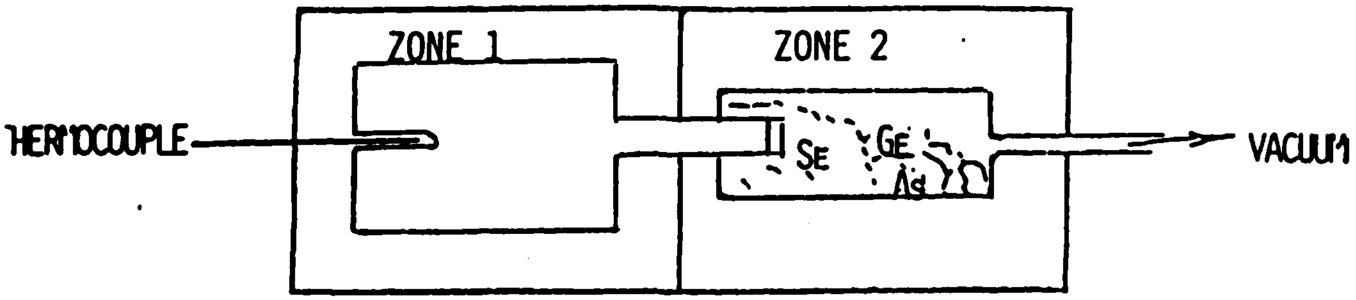
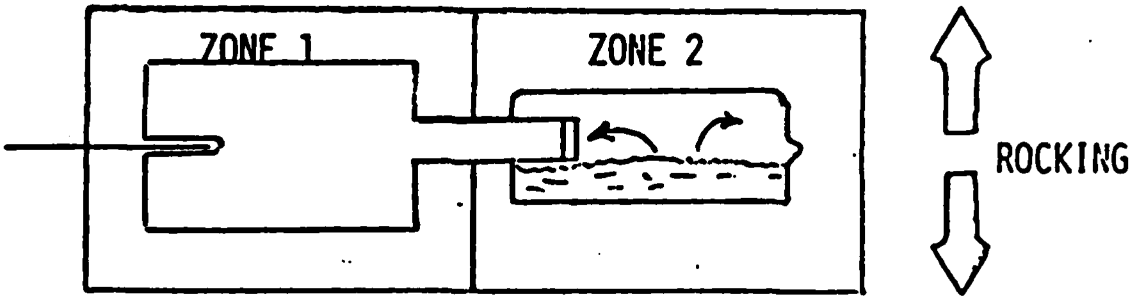


FIG. 6 OPTICAL TRANSMISSION OF Ga-DOPED CdTe

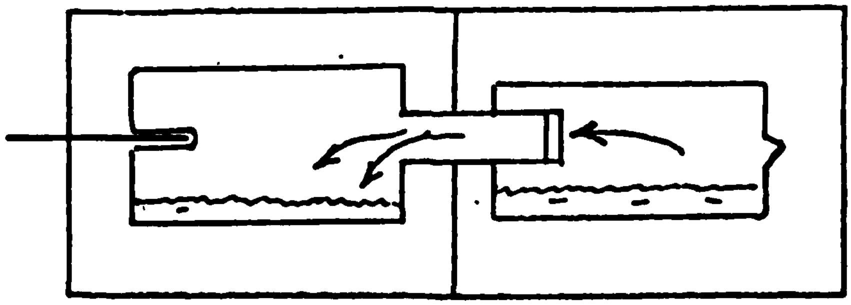
FIG. 7 GLASS PROCESS DIAGRAM



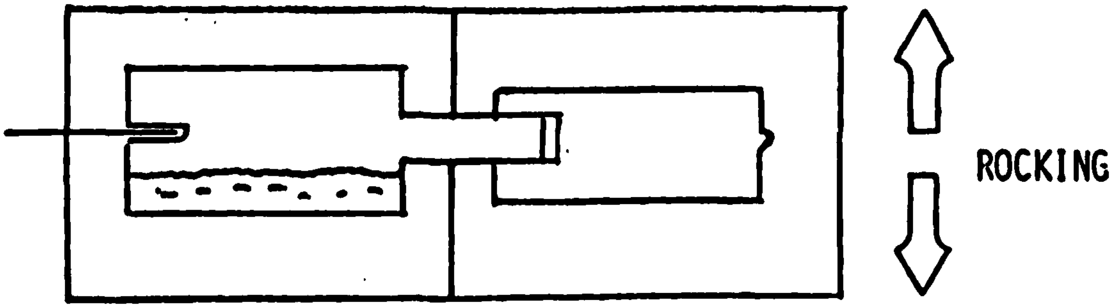
PURIFICATION



COMPOUNDING



DISTILLATION



CASTING

Rocking is stopped and the glass casting chamber cooled to allow transfer of the compounded glass into the casting chamber. Distillation occus through a porous quartz filter which removes all particulate matter. The distillation generally takes 12-15 hours. The amount of material passed through the frit varies depending upon diameter and thickness. A 6" diameter plate 2" thick requires about 4Kgms of glass while a 8" diameter plate 2" thick requires 7Kgms of material. It is interesting to note that the purity of the finished material improves with quantity prepared. The total amount of impurities from quartz walls, vaccuum system. etc. remains constant while the ending concentration decreases with increase in mass. The distilled glass is mixed by rocking. The glass is then allowed to cool while rocking down to the casting temperature range. Rocking is stopped and the furnace leveled. The glass is rapidly cooled using compressed air to the anneal range 370 ° C. The glass is annealed 6-8 hours before being allowed to cool to room temperature.

AMTIR-I glass is compounded in very unique and valuable high purity quartz containers. Casting chambers 6", 8" and 10" in diameter are routinely prepared. Methods have been worked out to open the chambers with a diamond saw so that the cast plate may be removed without breaking. The chambers are cleaned and resealed for reuse. The compounding tubes are not saved. The impurities within the high purity reactants are left behind during the distillation. The residues are sometimes quite large indicating the effectiveness of the method in preparing high purity solid materials.

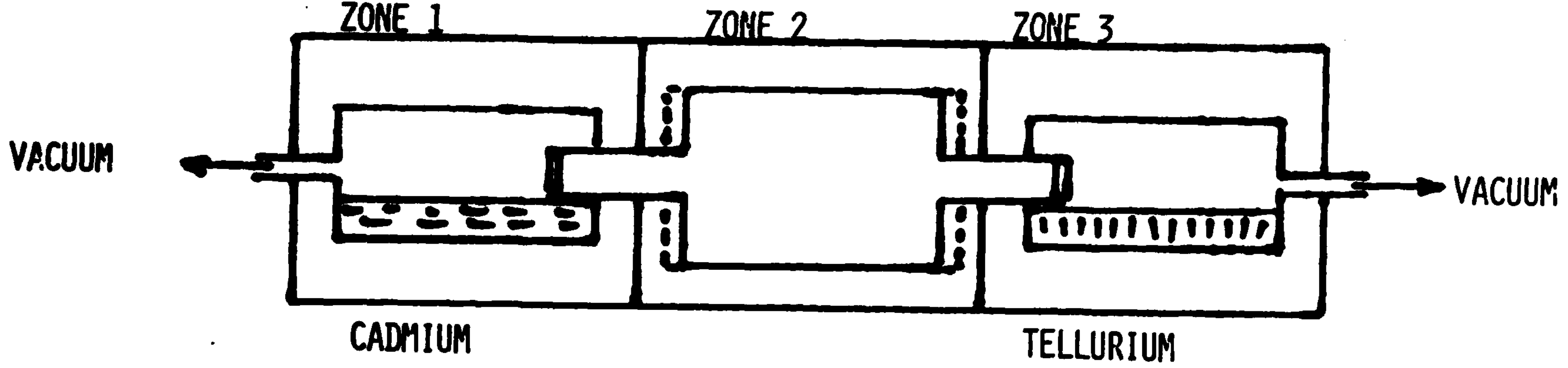
B. Modification for Vapor Growth of CdTe

A three chamber zone approach would be required if the program goals were to be met. A diagram depicting the modification of the AMTIR method is shown in figure 8.

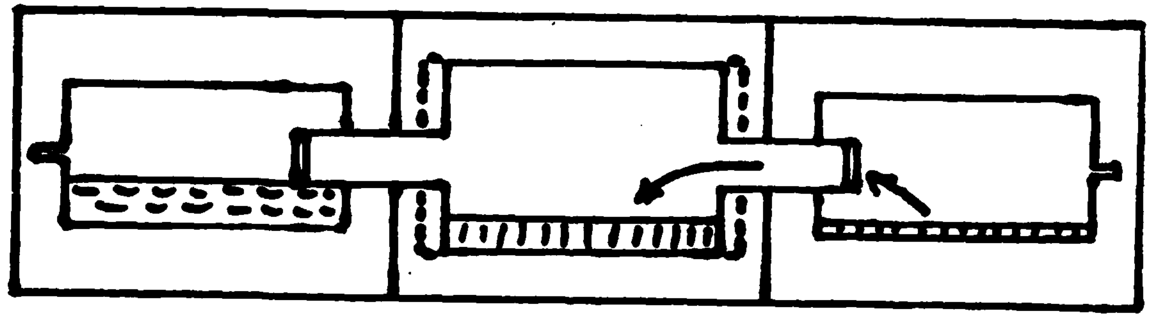
The elements are melted and purified while being pumped from both ends. After this step is completed and the chambers sealed, one element is transferred into the plate chamber and condensed as a liquid. In this case, cadmium is transferred first. Condensation as a liquid in the bottom of the chamber insures CdTe plate growth will occur where it is most desired. Notice the plate chamber is wrapped with quartz wool insulation to help establish the desired temperature gradients.

The second step involves compounding CdTe by transferring tellurium vapor into the chamber. After the melt is compounded, air may be blown on the bottom of the chamber to promote crystal growth from the center and the bottom of the melt. The procedure, equipment used and early results were reported in Technical Report No. 3.

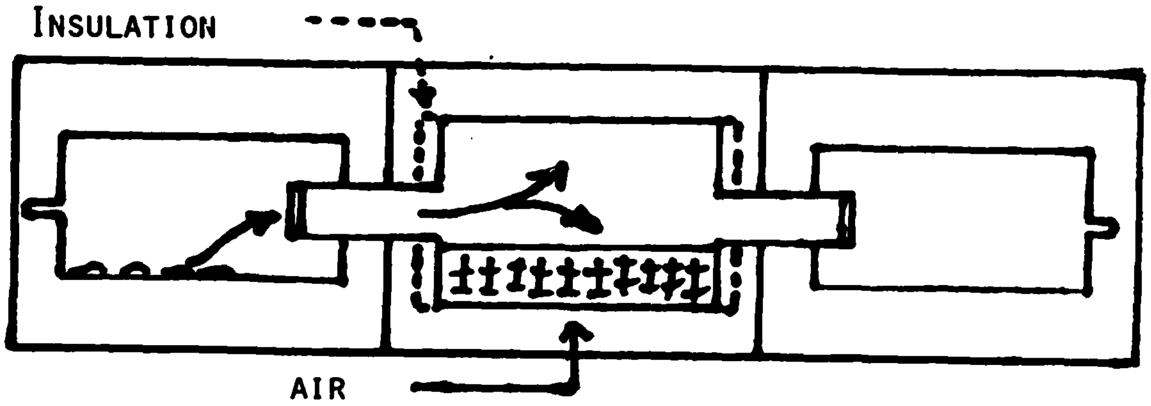
FIG. 8 THREE ZONE MELT GROWTH PROCESS



REACTANT PURIFICATION



TELLURIUM TRANSFER



CADMIUM TELLURIDE GROWTH

IV. RESULTS FOR THIS QUARTER

A. CdTe Plate Fabrication

During this reporting period a total of eight plate fabrication runs were made. The conditions and results of these runs are summarized in Table I from No. 51 through No. 58 inclusive. Both attempts at 10 inch diameter plates failed due to quartz rupture which occurred in both cases before maximum temperature had been achieved. The same result was obtained from one 8 inch attempt, the quartz chamber imploding on pump down. However, considerable insight into the freezing process was gained from the other four runs from which plates were obtained. The last two of these plates were a full one inch thick with large area crystals and showed no evidence of voids, gross inclusions or dendritic growth. We believe that our ability to reproduce these results is evidence that the freezing process is understood and under control. These plates will be discussed in detail.

Plate #52

This plate was compounded in an 8 inch diameter quartz chamber by the usual procedure (see 7th Quarterly Report) from 5 - nines grade cadmium and tellurium. The cadmium was lightly etched in HCl, rinsed in deionized water, and air dried prior to loading. The tellurium was loaded in the "as received" condition in the form of broken pieces. The total charge weight was 3330 g and the elements were loaded in stoichiometric quantities.

The total temperature program essentially followed that shown in Figure 9 and the central chamber was insulated on the sides and top. The cooling air flow was directed against the bottom surface of the chamber at a flow of approximately one liter/min. at the appropriate time. The plate, when it was removed from the chamber appeared to be solid with very little, if any, indication of dendritic growth. After grinding however, the upper surface and the bottom surface were completely different in appearance. While the lower surface (first to freeze) showed the usual large area grain growth, the upper surface showed very small grain growth (approx. 1/4 inch size) as if freezing had occured rapidly or perhaps the liquid had super cooled. After the plate was cut in half it was observed that a large cavity was present in the center of the plate which suggested that the plate was solidified in two half sections, one freezing from the bottom up and the other freezing from the top down. The center cavity is where the two sections met. The bottom half of this plate was cut into one inch squares, approximately 1/4 inch thick, lapped, polished and used for subsequent heat treating experiments.

TABLE 1. THREE CHAMBER MELT GROWTH RESULTS

RUN NO.	TYPE	SIZE	CONDITIONS	RESULTS
26	Solution	2Kgms.6"	Cd 45 Te55, 1090-800 Air 24Hrs.	Lg. Grain, 1 layer
27	"	6Kgms.8"	" "	Cd did not transfer.
28	"	" "	" "	" "
29	"	4Kgms.8"	Cd45 Te55, 1090-800, 24Hrs. Air	Most of Cd did not transfer
30	"	2.5Kgms.8"	Cd45 Te55, 1050-800, 24Hrs. Air, Cd transferred first	Small grain plate 0.3" thick
31	"	" "	Cd45 Te55, 1050-800, 24Hrs. Tellurium transferred while Cd cooled	Most of Cd did not transfer, thin plate
32	"	" "	Cd 45 Te55, 1075-800 Air,	Thin plate, most Cd did not transfer
33	"	" "	Cd45 Te55, 1075-800	Cd did not tranfer, poor quality
34	"	" "	Cd45 Te55, 1075-800 Air,	Small grain, thin plate
35	"	" "	Cd45 Te55, 1075-800	Cd did not transfer
36	"	" "	Cd transferred first, used check valve	Quartz failed
37	"	" "	Cd transferred first 1085/cooled, 6°C/HR	Good plate
38	"	" "	Same	Excellent plate
39	"	" "	Cd48 Te52, 1095, 3°C/HR	Good plate
40	"	3.3Kgms.8"	Cd42 Te58, 1050, 3°C/HR	Good plate
41	"	4.8Kgms.8"	Cd45 Te55, 1085, 5°C/HR	Good plate
43	"	" "	Cd45 Te55, 1060, 3°C/HR	Excellent plate
44	"	" "	Cd45 Te55, 1060, 3°C/HR New Furnace	Fair plate
45	"	" "	Repeat of 44	Excellent plate
46	"	7.7Kgms.10"	Cd45 Te55, 1060, 3°C/HR	Quartz failed

(CONTINUED)

RUN NO.	MELT COMP.	SIZE	CONDITIONS	RESULTS
47	55% Te 45% Cd	10 inch 7.4Kg	Air Cooled	Plate intact - Two Regions of Crystal Growth Upper Plate Region Dendritic
48	55% Te 45% Cd	10 inch 7.4Kg	Air Cooled	Same As Above
49	55% Te 45% Cd	6 inch 2.4Kg	Air Cooled Seeded Melt	Large Area Single Crystals, Upper Half of Plate Dendritic
50	50% Te 50% Cd	8 inch 3.1Kg	Air Cooled Seeded Melt	Large Area Single Crystals, No Dendritic Growth, Good IR Transmission Finished Plate 11mm Thick
51	50% Te 50% Cd	10 inch 5.5Kg	Insulated Chamber Unseeded	Chamber Ruptured Before Compounding
52	50% Te 50% Cd	8 inch 3.3Kg	Insulated Chamber Seeded Melt	Cavity In Center Of Plate Across Entire Diameter Will Cut One Inch Squares For Heat Treatment
53	50% Te 50% Cd	10 inch 5.5Kg	Insulated Chamber Unseeded	Chamber Ruptured Before Compounding Completed
54	50% Te 50% Cd	8 inch 3.3Kg	Insulated Chamber Seeded Melt	Chamber Imploded During Initial Pump Down
55	50% Te 50% Cd	8 inch 3.3Kg	Insulated Chamber Seeded Melt	No Plate Obtained Cadmium Had Not Transferred
56	50% Te 50% Cd	6 inch 3.3Kg	Insulated Chamber Top & Bottom Seeded Melt	One Inch Thick Plate Obtained-Very Thin Void Across Upper 1/3 Of Plate

(CONTINUED)

IN NO.	MELT COMP.	SIZE	CONDITIONS	RESULTS
57	50% Te 50% Cd	6 Inch 3.3Kg	Insulated Chamber Increased Air Flow	One Inch Thick Plate Obtained-Large Grain Areas-No Voids
58	50% Te 50% Cd	6 inch 3.3Kg	Insulated Chamber Off-Set Air Flow	One Inch Thick Plate Obtained-No Voids

Figure 9

CENTER CHAMBER (T_2) TEMPERATURE PROGRAM

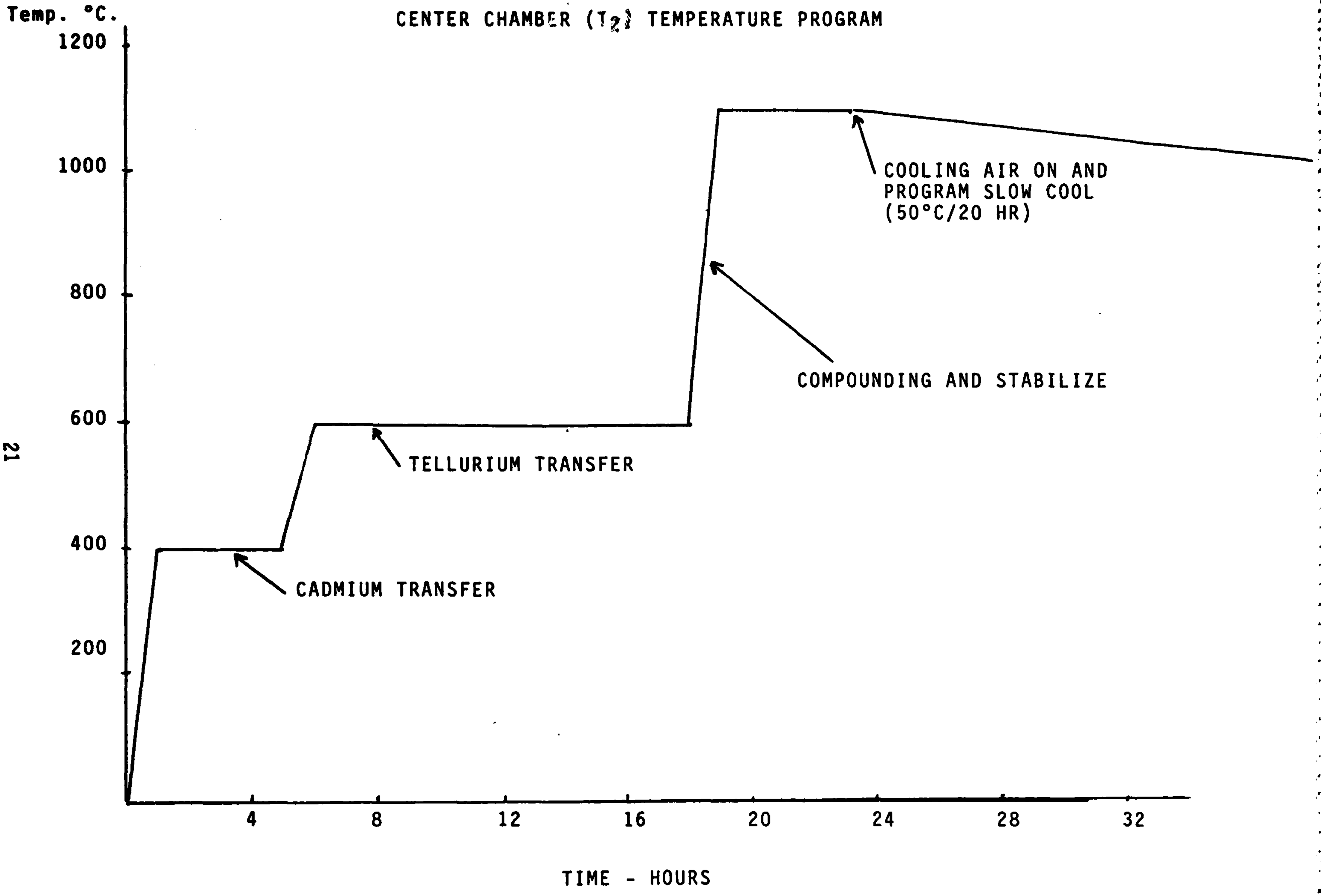


Plate #56

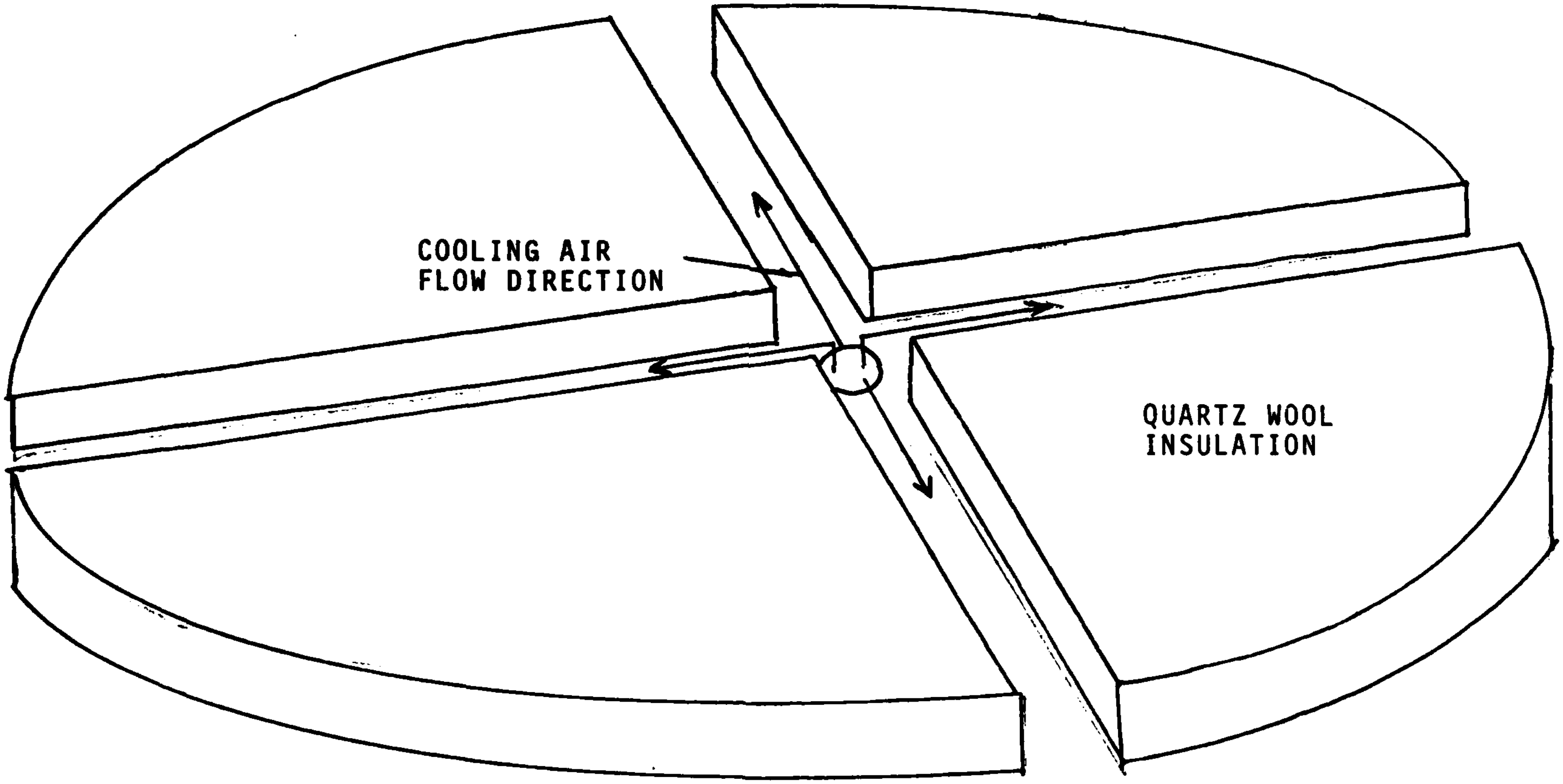
This plate was compounded from stoichiometric quantities of cadmium and tellurium for a total weight of 3338 g. Since the central chamber was only 6 inches in diameter sufficient melt was present to prepare a plate slightly greater than one inch in thickness. The top surface of the chamber was insulated with quartz wool somewhat more than the previous run and the cooling air flow on the bottom of the chamber was maintained at 2 liter/min. In addition, a third thermocouple was placed under the bottom of the chamber at a position corresponding to approximately half the radius. In this way we could measure the temperature gradient from the top surface to the bottom surface of the melt. In addition, the insulation support on the bottom of the chamber was channeled (see Figure 11) in an attempt to increase the temperature gradient across the thickness of the melt. After compounding the melt, a temperature gradient of 12 - 15 was measured after the cooling air flow was turned on. The resulting plate was one inch thick after lightly grinding the upper and lower surfaces to achieve parallelism. Although no cracks or voids were visible on the outside surfaces of the plate, it did not transmit IR. Again, the crystallites on the bottom surface were large compared to those on the top surface. A cross section of this plate is shown in Figure 11 . The very thin voided region, we conclude, is a result of freezing which occurred from the top downward while the bottom was freezing in an upward direction.

Plate #57

This run was made in almost exact duplication of the previous run for plate #56. The chamber diameter was 6 inches and the total stoichiometric charge weight was 3347 g. The same channeled insulation was again used on the bottom of the chamber, however, on this run the cooling air flow was increased to 5 liter/min. As in most previous runs the cooling air flow was directed on the outer surface of the center of the plate where the seed cavity is located. Although single crystal seeds cut from previous samples were placed in the seed cavity before compounding, there is little doubt that the seed probably dissolves during the compounding process and the seed cavity serves only as a nucleation origin site. The run was made following a normal temperature/time cycle and a gradient of 12° C was measured between the lower thermocouple (bottom of plate) and middle thermocouple (adjacent to top of plate). The resulting plate showed good IR transmission even before grinding and polishing indicating the absence of voids or large inclusions. (Figure 12) After grinding and polishing the finished plate weighed 2850 g and measured exactly one inch thick. The size of the single crystal regions was the same on both the top and bottom surfaces indicating growth

Figure 10

COOLING AIR FLOW PATTERN ON BOTTOM OF GROWTH CHAMBER



Cross section of plate No. 56 thin void region indicates two freezing patterns.

Figure 11

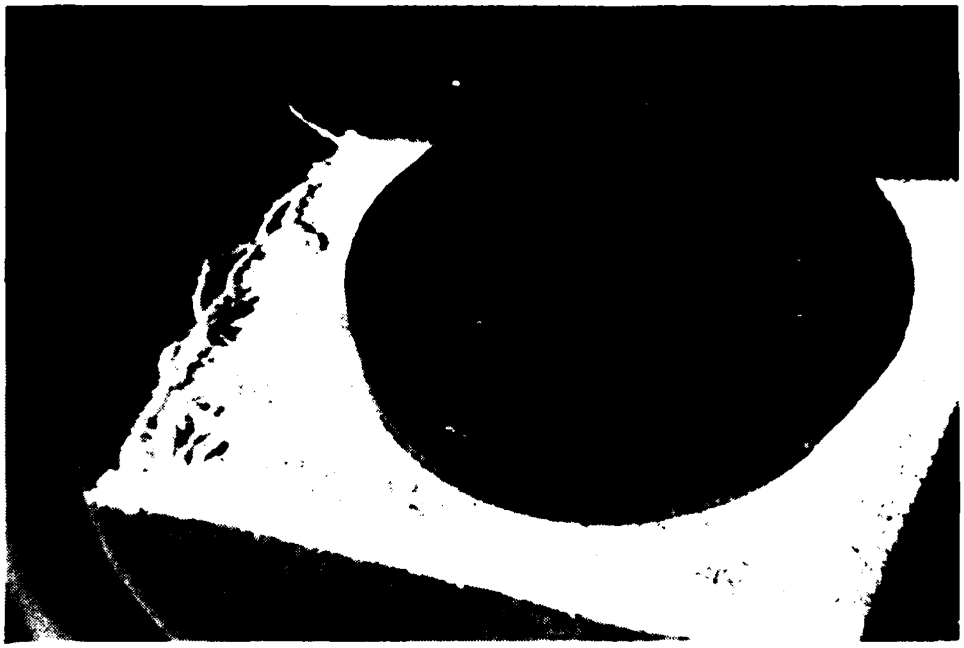


Plate #57 - As grown condition - before grinding

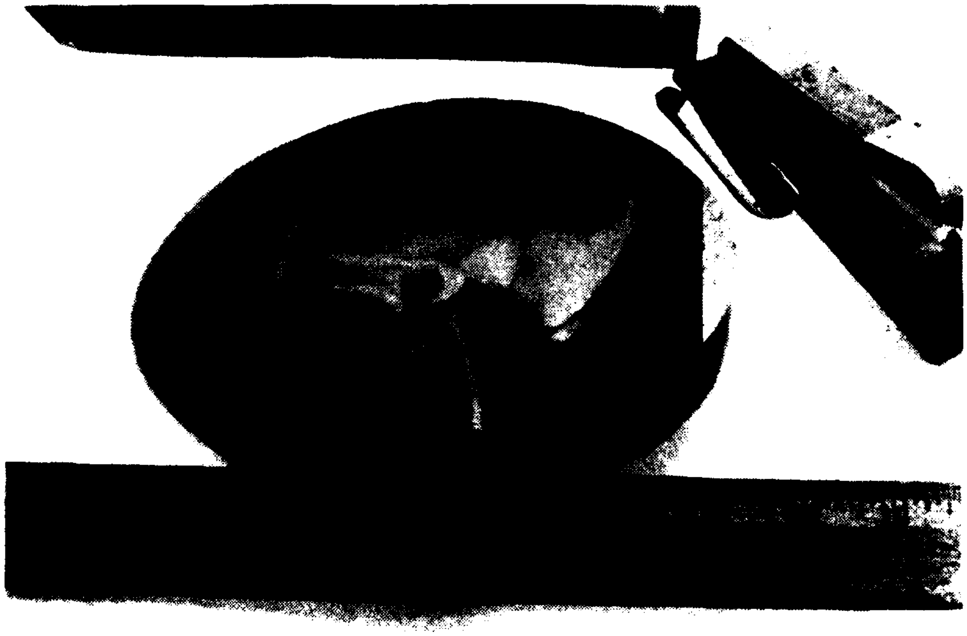


Plate #57 - After grind, lap and polish
Figure 12

by a single freezing process from one origin. Distinct crystal shapes could also be identified on both surfaces indicating that crystal growth was largely in the vertical direction. Although a single crystal seed (near 110) had been placed in the seed cavity it was noted that the orientation of the single crystal regions in the center of the plate did not correspond to that of the seed. (Figure 13)

Plate #58

This run was also made using a 6 inch diameter chamber and following the same charge weight, temperature cycle and cooling air rate as the previous run. The only change made was in the pattern of the cooling air flow. (Figure 14) The air flow was directed against the extreme edge of the chamber (instead of the center) in an effort to provide a longer linear growth direction. The resulting plate was slightly over one inch thick and as before, exhibited IR transmission in the as grown state indicating the absence of voids or large inclusions. The size of the single crystal areas however was not noticeably larger than the previous plate in spite of the different freezing configuration. The largest of the single crystal regions of this plate were cut out, oriented on the (111) and wafered into 50 mil thick substrates. (Figure 15)

B. Heat Treatment

The first samples for heat treatment studies were cut from plate #52. The samples measured approximately 1" X 1" X 1/4". The samples were polycrystalline, mechanically polished on both sides, and etched-polished in bromine-methanol (1:10) in a rotating beaker for 10 min. before being placed in the heat treating chamber. The chamber, constructed of quartz in two sections is shown in Figure 16. Approximately 5.5 g of 5 - nines grade cadmium were placed in the chamber along with the samples which were run in triplicate. The heat treatment was carried out in a 2 - zone furnace. The cadmium zone was maintained at 765 °C. (approx. one atmos.) while the CdTe samples were maintained at 800°C for approximately 70 hours. The samples were examined and evaluated under an IR microscope before and after the heat treating process. Sketches were made of various areas of each sample.

A second set of samples was heat treated in a similar manner under 5 - nines tellurium (5 g chunk). Again the heat treatment was carried out for 70 hours at 800 ° C for both the samples and the tellurium source.

Figure 13

SEEDING ARRANGMENT FOR LARGE DIAMETER CdTe PLATES

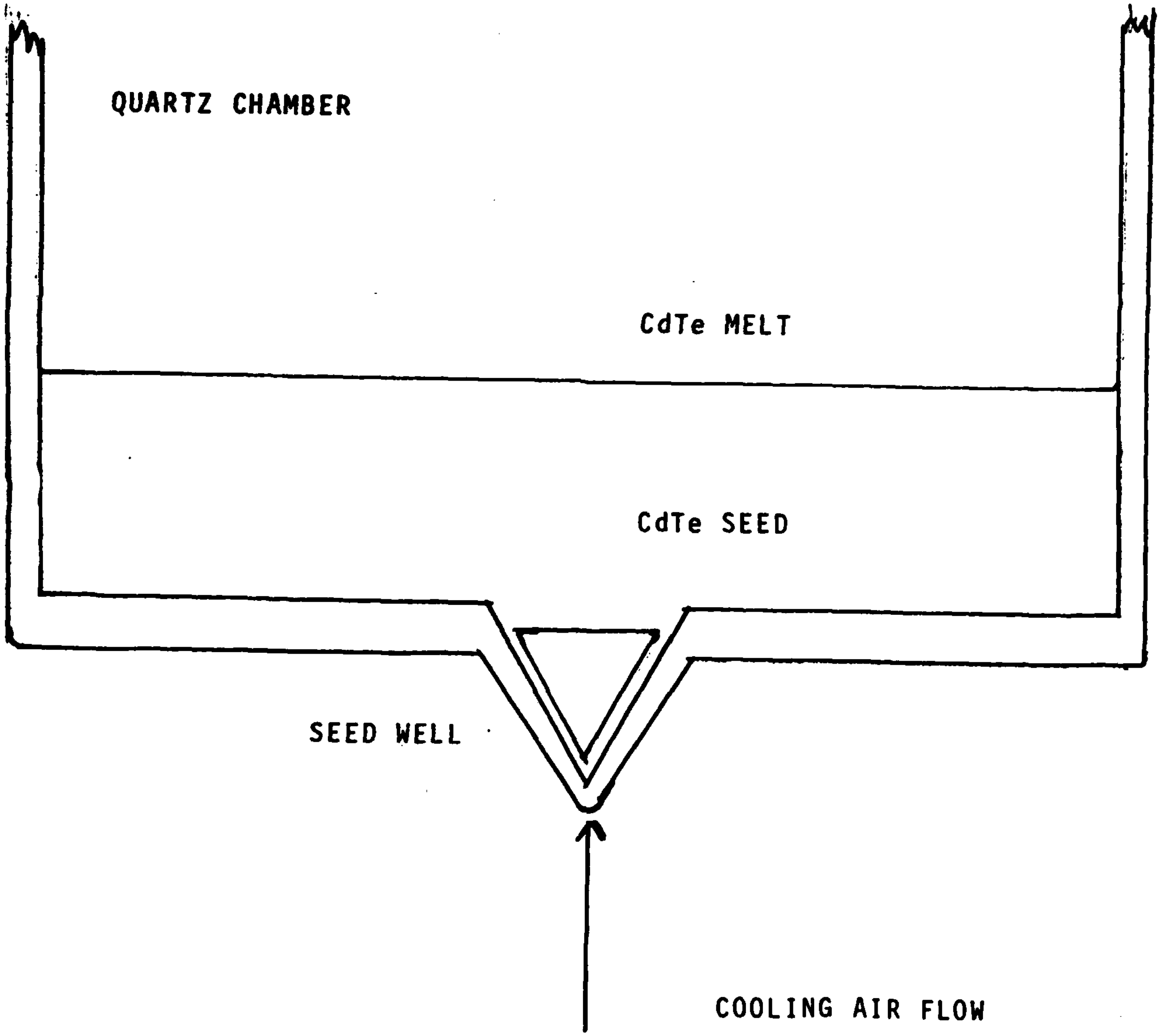
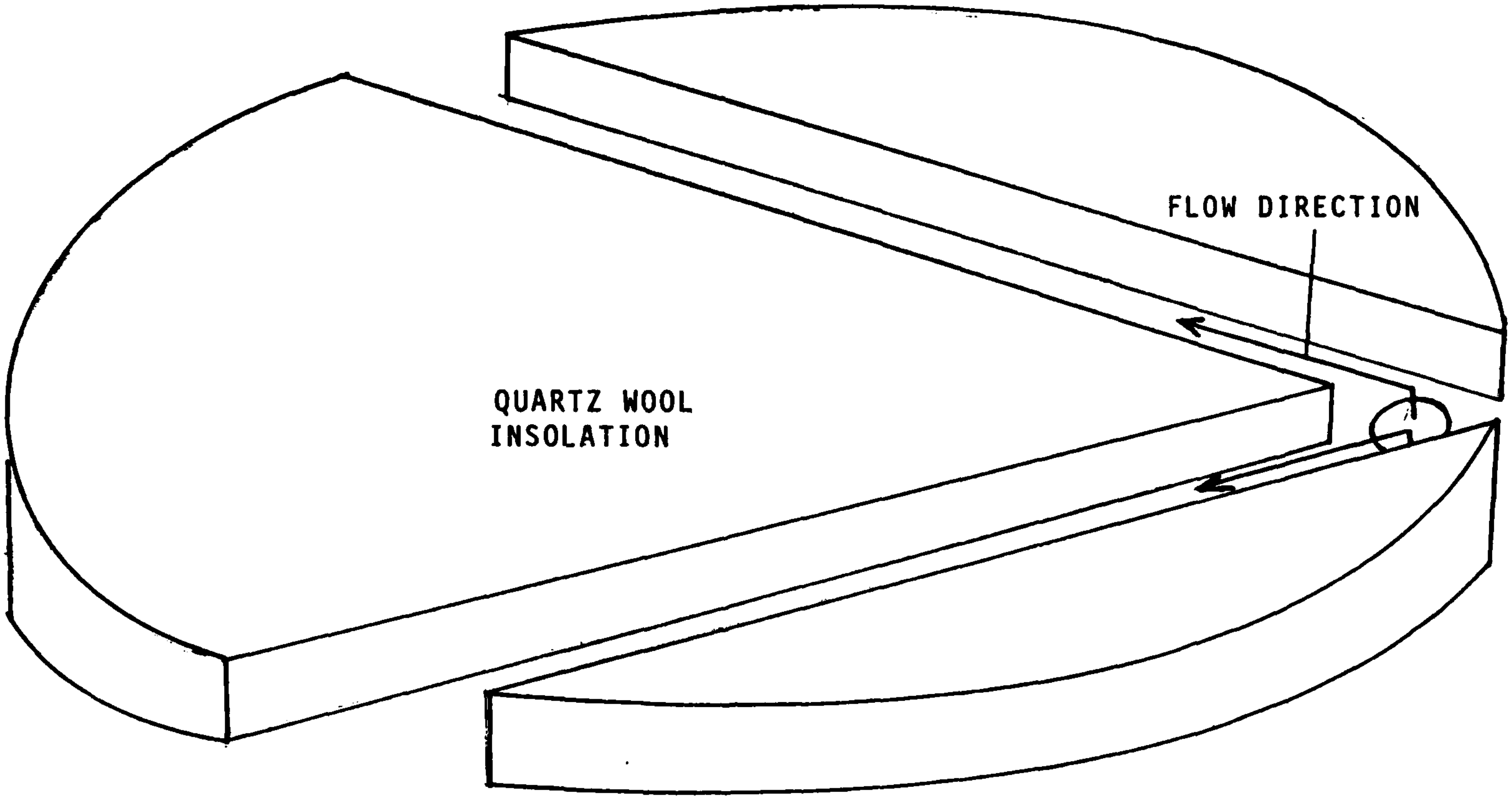


Figure 14

ALTERNATE COOLING AIR FLOW PATTERN - BOTTOM OF CHAMBER



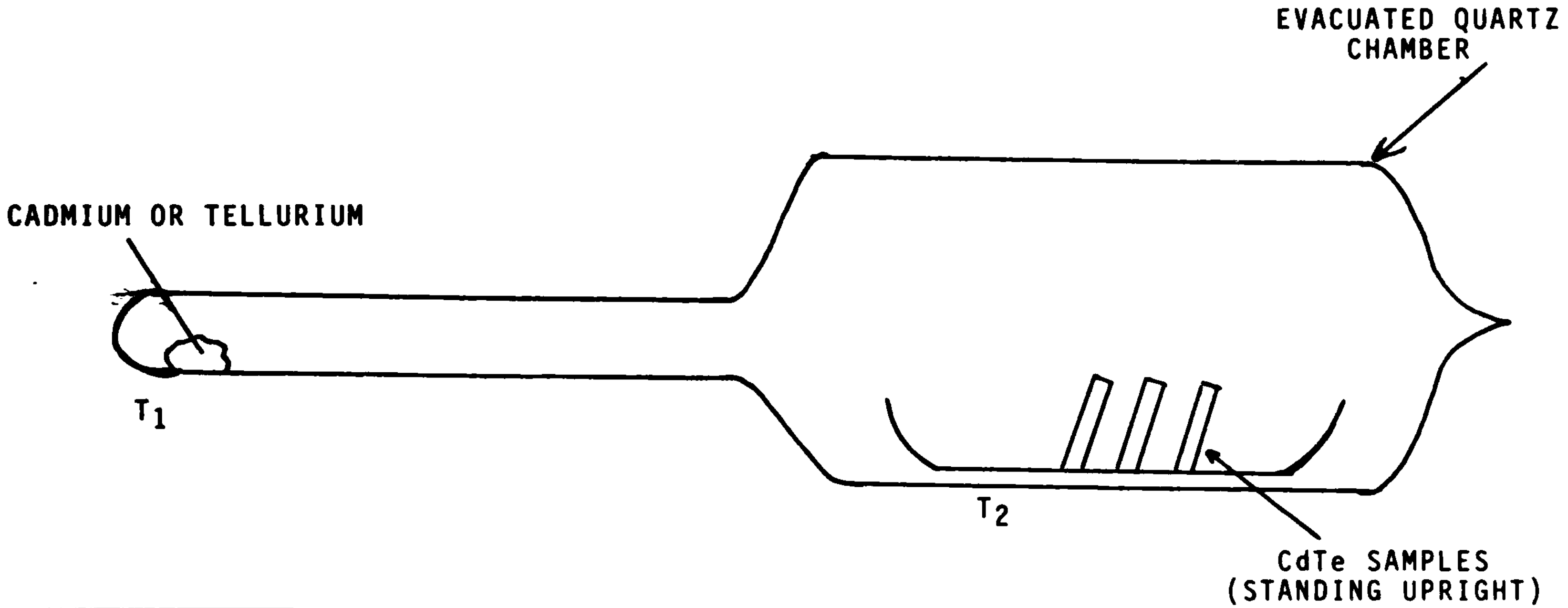
Examples of CdTe (111) oriented substrates cut from recent plates.

From plate #56

From plate #57

Figure 15

HEAT TREATING OF CdTe



	Cd	Te
T_1 =	765°C	800°C
T_2 =	800°C	800°C

TIME = 70 HOURS

Figure 16

The cadmium vapor heat treatment showed the greater "before/after" change. The grain boundaries which were thick and opaque before heat treatment became very fine and barely visible under IR transmission. The surface in general, remained shiny, however, at the grain boundary a black crusty deposit formed as if excess tellurium had exuded out of the sample. Regions which showed a heavy concentration of opaque precipitates under IR microscopy before heat treatment became distinctly clearer after. Finally, thermal probing showed that samples which had been semi-insulating before heat treatment had converted to low resistivity with p-type conductivity after cadmium heat treatment.

Under tellurium vapor, a distinct change in surface morphology was observed. In general, pits were formed which showed crystallographic characteristics. The appearance of the grain boundaries under IR microscopy showed very little, if any, change in appearance and all samples which had been semi-insulating before heat converted to low resistivity with n-type conductivity after tellurium heat treatment.

A third set of samples, one inch in thickness are currently under going heat treatment experiments. Quantitative IR transmission measurements will be made before and after heat treatment and the results presented in the next report.

C. Liquid phase epitaxy of HgCdTe

A single LPE run was carried out in a 2 - zone furnace using (111) oriented single crystal CdTe substrates. A melt composition was formulated from 0.217, 0.0092 and 0.774 atom fraction respectively of mercury, cadmium and tellurium (5) all of 5 - nines purity. As in the heat treatment studies, the mechanically polished substrates were further polished-etched in a 1:10 bromine-methanol mixture for 10 min. in a rotating beaker.

The samples were placed alongside the melt in a specially constructed quartz boat arrangement which could be rotated to cover and uncover the substrates with the melt. After loading, the chamber was evacuated and placed in the 2 - zone furnace. The mercury control zone was maintained at 250° C (0.1 atmosphere) while the melt was slowly raised to 500° C and maintained at that temperature for 2 hours to homogenize. The melt was then slowly cooled to 490° C at which temperature it was rolled over the substrates.

Slow cooling was allowed to continue from 490° C to 470 ° C over a 30 min. period. At 470° C the melt was rolled away from the substrates and the temperature allowed to drop to 270 ° C. The mercury control zone was then turned off and the samples allowed to anneal at 270 ° C for 24 hours.

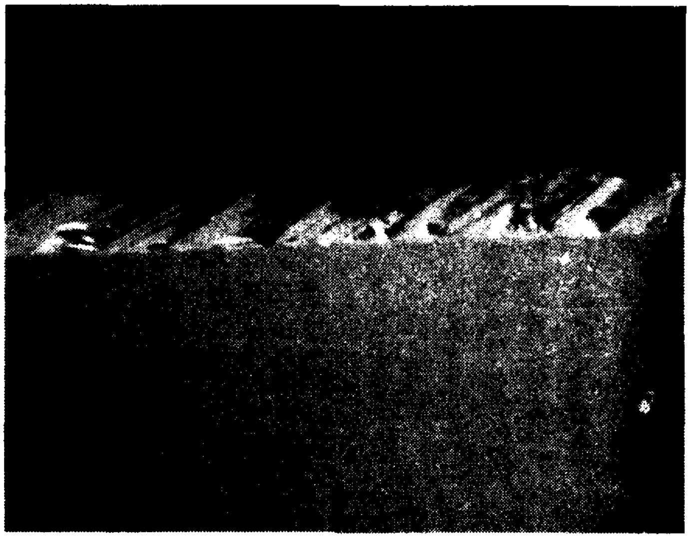
The resulting layer (Figure 17) was about 35 microns in thickness and clearly visible on the cleaved (110) edge of the sample. Etching was unnecessary. IR tranmission measurements showed a cut off at approximately 10 microns wavelength which corresponds to an X value of about 0.17 in the formula $Hg_{1-x}Cd_xTe$.

D. Substrate Preparation

During this reporting period a serious effort was made to develop techniques for preparing high quality (111) oriented substrates from the single crystal regions of the plates described previously. A goniometer head was obtained so that single crystal chunks "mined" from the plates could be mounted and oriented directly on the sawing fixture. In addition, a fixture was made so that the helium-neon laser used for optical orientation could be mounted directly on the wire saw used for wafering substrates. With this technique we estimate an orientation accuracy of ± 0.5 degree. (Figure 18)

Two methods for polishing substrates were examined. In the first method, lapped substrates were placed singly in a plastic beaker (400 ml) mounted at a 60°angle on a motor driven shaft. This technique is commonly used as a chemical polishing technique for other semiconductor materials such as silicon to produce a damage free surface since the polished wafer only comes in contact with the polishing solution. In this case a mixture of bromine-methanol in approximately a 1 to 10 ratio. Polishing time was about 10 - 15 min. during which time 1 - 2 mils of material are removed from each side of the wafer. This procedure works best however when the wafers are round in shape and can roll in the polishing solution as the beaker is rotated (about 60 rpm). The CdTe substrates however, were mostly rectangular in shape and did not rotate in the polishing solution. As a result, the polished surface while smooth and shiny was often not completely flat over the entire plane of the wafer.

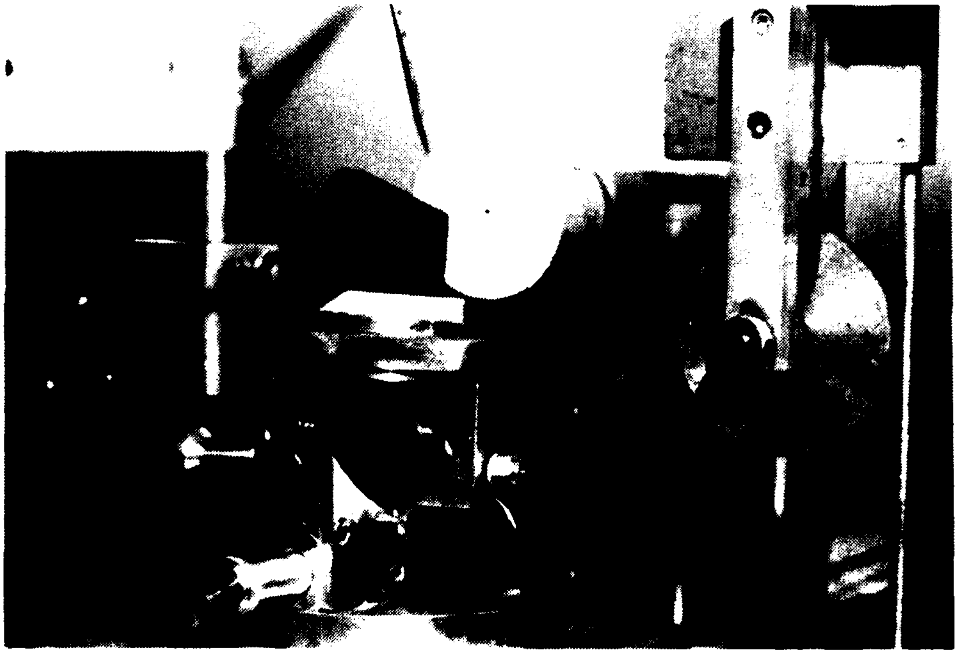
As an alternate method, substrates were waxed to a stainless steel plate in groups of 7 or 8 and lapped to produce a co-planar surface. The plate was then placed on a Strasbaugh polisher using a dacron pad soaked with a mixture of sodium hypochlorite and water, 1:1. Polishing time was approximately 30 min and a smooth specular surface was



Cross section of epitaxial layer on CdTe substrate - Layer thickness approx. 35 microns.

(Magnification 70X)

Figure 17



Goniometer - laser arrangement for crystal orientation on wire saw.

Figure 18

easily achieved. Although these surfaces are completely flat, shiny and free of grooves or scratches, contact with the dacron pad may induce some degree of surface damage. For this reason we believe a combination of the two techiques may be the best solution, that is; initial polishing with sodium hypochlorite solution on a dacron pad followed by a 2 - 3 min. bromine-methanol treatment in a rotating beaker.

V. PLANS FOR NEXT QUARTER

For next quarter we have at least three specific goals and plans for achieving them.

First, we will re-emphasize the seeding process in an attempt to get larger areas of single crystal. (A desirable but perhaps impractical goal would be to grow the entire plate as a single crystal) It's possible the dissolution of the seed could be prevented or delayed by controlling a small cooling air flow directly on the seed compartment during the entire compounding process. Also, we will consider changing the temperature profile during the freezing process to achieve a slower growth rate during the critical range of 1098° C to 1090° C.

Second, we will continue the heat treating experiments in an attempt to improve the optical transmission. Recent results have shown that beat treatment under both cadmium as well as tellurium vapor will be required but time and temperture factors have not yet been optimized.

Finally, a prism measuring approximately 1" X 2" X 1/2" thick has been cut and polished for a precise (five figures) refractive index measurement. This work is in progress and will be completed during the next reporting period.

REFERENCES

1. "Phase Equilibria and Semiconducting Properties of Cadmium Telluride" By: D. de Nobel Phillips Research Reports 14 361-399 (1959)

2. "Research on Improved II-VI Crystals" By: L. R. Shiozawa and J. M. Jost, Clevite Corporation, Cleveland, Ohio Contract No. F33615-68-C-1601-P002 January 1971.

3. "The Application of Physical Vapor Deposition to Semiconductor Materials for Use as High Power Infrared Windows" By: L. R. Shiozowa, J. M. Jost and D. A. Roberts, Gould Laboratories, Cleveland, Ohio Contract No. F33615-71-C-1777 September 1973.

4. "Partial Pressures in the CdTe and SeTe Systems" R. F. Brebrick, J. Electrochem Sec. 118 2014 (1971)

5. Melt composition suggested by Carlos Castro, Texas Instruments, Inc.